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THEORY OF X-RAY EMISSION SPECTRA IN Ce COMPOUNDS

S. Tanaka, Y. Kayanuma and A. Kotani

Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan

Abstract. - X-ray emission spectra (XES) corresponding to the Ce 5p → 3d transition in insulating Ce compounds are studied theoretically with the impurity Anderson model. It is shown that the XES reflects the dynamical relaxation through the hybridization between 4f and valence band states, as well as the lifetime of 3d core hole.

1. Introduction

X-ray emission (XES) is one of the most fundamental X-ray processes as X-ray absorption (XAS) and X-ray photoemission (XPS), and is expected to give important information of f and d electron states in magnetic materials. However, much less theoretical works have been done for XES than for XAS and XPS. Recently, we have presented a theory of XES corresponding to the 4f → 3d electronic transition in La compounds [1], and in this paper we extend the theory to the 5p → 3d XES of insulating Ce compounds, such as CeF₃ and Ce₂O₃. We use the impurity Anderson model with a filled valence band, which has been used successfully in the analysis of XAS and XPS for these materials [2, 3].

We consider the situation where a Ce 3d core electron is excited to a high energy ionization continuum by absorbing a monochromatic incident X-ray and then a Ce 5p core electron makes a transition to the 3d level by emitting an X-ray photon. When the 3d core hole is created, a dynamical relaxation of Ce 4f state occurs owing to a core hole potential \(-U_{fc}(3d)\) and a hybridization \(V\) between the 4f state and the valence band. Since the lifetime of the 3d core hole (which is determined mainly by the Auger decay) is comparable with the characteristic time of the dynamical relaxation due to \(V\), it is important to treat the whole process as a coherent second order optical process. It will be shown that the competition between the lifetime of the 3d core hole and the dynamical relaxation of the 4f state affects strongly the XES spectral features. The calculated XES will also be compared with available experimental data.

2. Model

We consider a system consisting of a Ce 4f level (with energy \(\varepsilon_f\)), the filled valence band (\(\varepsilon_v\)) of anions, and Ce 3d and 5p core levels (\(\varepsilon_{3d}\) and \(\varepsilon_{5p}\)). The 4f-state interacts with the valence band through the hybridization \(V\). The Hamiltonian of our system is given by

\[
H = \sum_{kv} \varepsilon_k a_k^+ a_k + \frac{e^2}{V} \sum_{i=1}^{\Gamma} a_i^+ a_i + \varepsilon_{3d} a_{3d}^+ a_{3d} + \varepsilon_{5p} a_{5p}^+ a_{5p} + \frac{1}{N} \sum_{kv} \left( a_{kv}^+ a_{kv} + a_{kv}^+ a_{kv} \right) + U_{fc}(3d) \left( 1 - a_{3d} a_{3d} \right) + U_{fc}(5p) \left( 1 - a_{5p} a_{5p} \right) \sum_{i} a_{i}^+ a_{i},
\]

where \(a_i\) (\(i = k, f\)) and \(a_j\) (\(j = 3d, 5p\)), respectively, denote the annihilation operators of an electron in the state (\(i, \nu\)) and \(j\), where \(\nu\) denotes the combined index to specify both f orbital symmetry and spin one (\(\nu \approx 1 \sim 14\)). The orbital and spin degeneracies with respect to 3d and 5p states are neglected. \(U_{fc}(3d)\) and \(-U_{fc}(5p)\) represent the intra-atomic 4f-4f Coulomb interaction, the 3d and 5p core hole potentials, respectively.

The intensity of the radiation emitted by the 5p → 3d electronic transition is given by

\[
S(\omega) = \int \frac{1}{H + \varepsilon - E_g - \Omega - i\Gamma(3d) a_{3d} |g\rangle^2} \times \frac{\Gamma(5p)}{\pi} \left( \Omega + E_g - \omega - \varepsilon - E_j \right)^2 + \Gamma(5p)^2, \tag{2.2}
\]

where \(\Omega\) and \(\omega\) are energies of the incident and emitted photons, respectively. \(|g\rangle\) is the ground state of \(H\) with energy \(E_g\), and \(|j\rangle\) is the final state (i.e., the eigenstate of \(H\) with the 5p core hole) with energy \(E_j\). \(\Gamma(3d)\) and \(\Gamma(5p)\) represent the damping arising from the lifetime of the 3d- and 5p-core holes, respectively. The spectra \(S(\omega)\) are calculated by exactly diagonalizing the Hamiltonian in the sub-space containing 4f⁰, 4f¹, 4f², and 4f³ configurations and for a finite system where \(\varepsilon_k\) are taken as

\[
\varepsilon_k = \varepsilon_0 - \frac{W}{2} + \frac{W}{N} \left( k - \frac{1}{2} \right), \quad k = 1, 2, ..., N \tag{2.3}
\]

where \(\varepsilon_0\) and \(W\) are the center and the width of the valence band, respectively. The value \(N\) is taken to be so large that the calculated spectra are well converged.
3. Results and discussions

In figure 1, we show the $5p \rightarrow 3d$ XES of CeF$_3$ calculated for various values of $U_{fc}(5p)$ and $\Gamma(3d)$. The other parameter values are taken as those determined by the analysis of the 3d-XPS [2], the valence XPS [3] and so on; $W = 3.0$ eV, $\epsilon_f^0 - \epsilon_v^0 = 4.0$ eV, $V = 0.53$ eV, $U_{fi} = 8.0$ eV, $U_{fc}(3d) = 11.3$ eV, $\Gamma(5p) = 1.0$ eV.

The ground state of CeF$_3$ has the $4f^5$ configuration, but in the intermediate state with the 3d core hole then $4f^2$ state is strongly hybridized with the $4f^1$ state because of the reduction of the energy difference between these two configurations owing to the 3d core hole potential. In the final state with the 5p core hole, the hybridization between these configurations becomes much smaller, because the 5p core hole potential is much weaker than the 3d one. We denote the final states having mainly $4f^1$ and $4f^2$ configurations as $4f^1$ and $4f^2$ final states, respectively.

As shown in figure 1, the XES of CeF$_3$ has two main peaks corresponding to the $4f^1$ (higher energy peak) and the $4f^2$ (lower energy peak) final states. When $U_{fc}(5p)$ becomes smaller, the energy separation between these XES peaks becomes larger, since the energy difference between the $4f^1$ and $4f^2$ states becomes larger.

The most striking feature of XES is its dependence of $\Gamma(3d)$. Figure 1 shows that the intensity ratio of the higher energy peak to the lower energy one increases with increasing $\Gamma(3d)$. This feature arises from the competition between the lifetime decay ($\Gamma(3d)$) and the dynamical relaxation ($V$) in the intermediate state. When the dynamical relaxation is switched on in the intermediate state, the $4f^1$ configuration of the ground state starts to hybridize with the $4f^2$ configuration. If $\Gamma(3d) > V$, however, the dynamical relaxation is prevented by the short lifetime of the intermediate state, and the probability of the $4f^1$ final state increases with increasing $\Gamma(3d)$. In figure 1, a shoulder is also seen at high energy, in addition to the two main peaks, and it originates from some structure of the intermediate state, but we do not discuss it any longer in this paper.

Very recently, the experimental observation of the $5p \rightarrow 3d$ XES for CeF$_3$ has been made by Hayasi et al. [4] by the X-ray stimulation. The result is shown in the inset of figure 1. The calculated XES with $U_{fc}(5p) = 3.75$ eV and $\Gamma(3d) = 0.75$ eV is found to be in fair agreement with the experimental data. We can predict theoretically somewhat different features of the $5p \rightarrow 3d$ XES for Ce$_2$O$_3$ and CeO$_2$, and we hope they will be checked experimentally in future.

In this paper we have shown that XES gives important information on the relaxation process in the intermediate state, concentrating on the $5p \rightarrow 3d$ XES. It is to be mentioned that the $4f \rightarrow 3d$ XES gives also important information. In the $4f \rightarrow 3d$ XES, the 4f electron participates directly in the radiative process, so that the XES is quite sensitive to the difference in the 4f electron state. Furthermore, it is interesting to study the XES which follows the $3d \rightarrow 4f$ resonant excitation in order to make clear the dynamical relaxation process in the intermediate state.

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